

shown in Table 4.5.

**Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans**

#### 4.4 THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick

**Table 4.5 Dipole Moments of Selected Molecules**

Type of Molecule	Example	Dipole Moment, $\mu(\text{D})$	Geometry
<b>Molecule (AB)</b>	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H <sub>2</sub>	0	linear
<b>Molecule (AB<sub>2</sub>)</b>	H <sub>2</sub> O	1.85	bent
	H <sub>2</sub> S	0.95	bent
	CO <sub>2</sub>	0	linear
<b>Molecule (AB<sub>3</sub>)</b>	NH <sub>3</sub>	1.47	trigonal-pyramidal
	NF <sub>3</sub>	0.23	trigonal-pyramidal
	BF <sub>3</sub>	0	trigonal-planar
<b>Molecule (AB<sub>4</sub>)</b>	CH <sub>4</sub>	0	tetrahedral
	CHCl <sub>3</sub>	1.04	tetrahedral
	CCl <sub>4</sub>	0	tetrahedral

2022-23

and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

**The main postulates of VSEPR theory are as follows:**

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance

result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as **(i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.**

Table 4.6 (page 114) shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Table 4.7 (page 115) shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 4.8 (page 116) explains the reasons for the distortions in the geometry of the molecule.

As depicted in Table 4.6, in the compounds of AB<sub>2</sub>, AB<sub>3</sub>, AB<sub>4</sub>, AB<sub>5</sub> and AB<sub>6</sub>, the arrangement of electron pairs and the B atoms around the central atom A are : **linear,**

from one another.

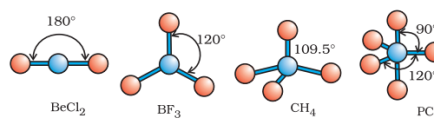
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

**The repulsive interaction of electron pairs decrease in the order:**

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions. These repulsion effects

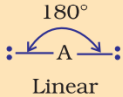
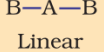
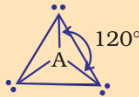
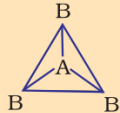
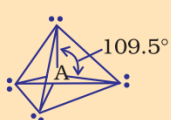
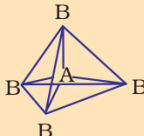
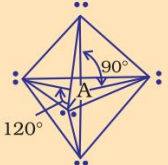
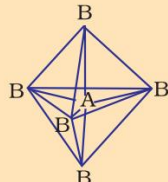
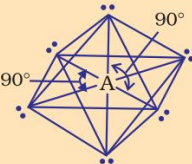
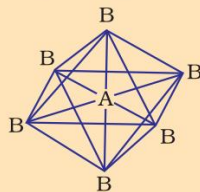
**trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral**, respectively. Such arrangement can be seen in the molecules like  $\text{BF}_3$  ( $\text{AB}_3$ ),  $\text{CH}_4$  ( $\text{AB}_4$ ) and  $\text{PCl}_5$  ( $\text{AB}_5$ ) as depicted below by their ball and stick models.



**Fig. 4.6** The shapes of molecules in which central atom has no lone pair

The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of *p*-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small. The theoretical basis of the VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion.

Table 4.6 Geometry of Molecules in which the Central Atom has No Lone Pair of Electrons

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 <p>Linear</p>	 <p>Linear</p>	BeCl <sub>2</sub> , HgCl <sub>2</sub>
3	 <p>Trigonal planar</p>	 <p>Trigonal planar</p>	BF <sub>3</sub>
4	 <p>Tetrahedral</p>	 <p>Tetrahedral</p>	CH <sub>4</sub> , NH <sub>4</sub> <sup>+</sup>
5	 <p>Trigonal bipyramidal</p>	 <p>Trigonal bipyramidal</p>	PCl <sub>5</sub>
6	 <p>Octahedral</p>	 <p>Octahedral</p>	SF <sub>6</sub>

**Table 4.7** Shape (geometry) of Some Simple Molecules/Ions with Central Ions having One or More Lone Pairs of Electrons(E).

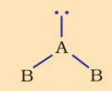
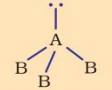
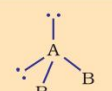
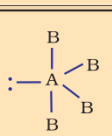
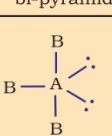
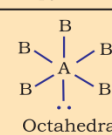
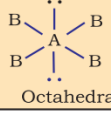
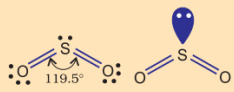
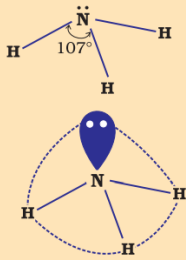
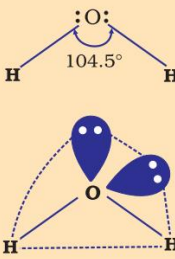
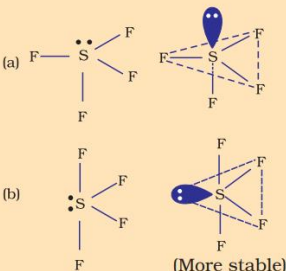
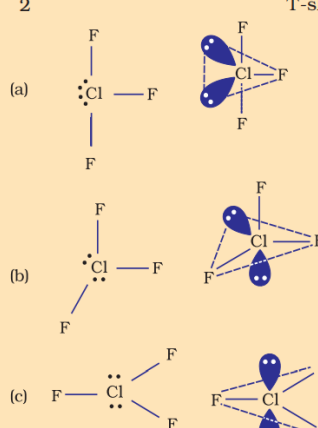
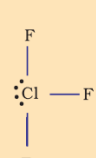
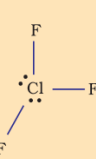

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
$AB_2E$	2	1	 Trigonal planer	Bent	$SO_2^{2-}$
$AB_3E$	3	1	 Tetrahedral	Trigonal pyramidal	$NH_3$
$AB_3E_2$	2	2	 Tetrahedral	Bent	$H_2O$
$AB_4E$	4	1	 Trigonal bi-pyramidal	See saw	$SF_4$
$AB_3E_2$	3	2	 Trigonal bi-pyramidal	T-shape	$ClF_3$
$AB_5E$	5	1	 Octahedral	Square pyramid	$BrF_5$
$AB_4E_2$	4	2	 Octahedral	Square planer	$XeF_4$

Table 4.8 Shapes of Molecules containing Bond Pair and Lone Pair

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
$AB_2E$	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°.
$AB_3E$	3	1		Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°.
$AB_2E_2$	2	2		Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°.
$AB_4E$	4	1		See-saw	In (a) the lp is present at axial position so there are three lp—bp repulsions at 90°. In (b) the lp is in an equatorial position, and there are two lp—bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw.

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
$AB_3E_2$	3	2	 <p>(a) </p> <p>(b) </p> <p>(c) </p>	T-shape	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped).